Electrochemical Analysis of Sulfaguanidine Azomethine and its Coordination Compound with Copper

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ABSTRACT

Sulfaguanidine azomethine and its coordination compound with copper were characterized by infrared spectroscopy. The cyclic voltammetric analyses of the ligand and complex were conducted at different scan rates and pH values. The ligand exhibits a single irreversible reduction wave in the electrochemical tests, while the Cu (II) complex exhibits a quasi-reversible wave. The kinetic parameters have been evaluated and discussed.

Keywords: 2-Acetyl-5-chlorothiophenesulfaguanidine (2-Ac-5-ClThSG), Cyclic voltammetry, Kinetic parameters, Irreversible reduction.

INTRODUCTION

The biological action of azomethines and their coordination compound shows diverse properties[1-4], analytical implications and impacts of corrosion inhibition [5-8]. The condensation of compounds having carbonyl group and primary amino group leads to formation of Schiff bases [9–13]. Biological systems, metals, semiconductors and polymers among the materials for which electrochemical reactions were known[14–21]. Electrochemical methods were heavily involved in many different fields, including materials science, analytical chemistry, solid-state chemistry, preparative chemistry, and microelectronics [22]. A typical three-electrode method like cyclic voltammetry and polarography were used to study electrochemical reactions. Cyclic voltammetry gained popularity as a method for learning about the reversible nature of electrode transfer processes and the production, reduction, and oxidation of intermediates[23-25]. This paper describes the synthesis of the Cu (II) complex with 2-Ac-5-ClThSG as well as spectroscopic and cyclic voltammetric investigations.

EXPERIMENTAL

Synthesis of 2-acetyl-5-clorothiophene sulfaguanidine: All the starting materials were utilized without further purification because they were analytical grade and the purest accessible. Sulfaguanidine and 2-acetyl-5-clorothiophene are purchased from TCI. 2-Acetyl-5-chlorothiophene sulfaguanidine (2-Ac-5-ClThSG) was made by reaction of 0.1 M 2-acetyl-5-

chlorothiophene with a sulfaguanidine in a 1:1 molar ratio using ethyl alcohol as solvent. The above solution is then heated for approximately 4:30 hours at 45°C. The resulting product was then dried with ethanol and purified. Once recrystallized in ethanol, the brown solid crystals were recovered. The findings indicated a melting point of 175°C and a yield of 68%.

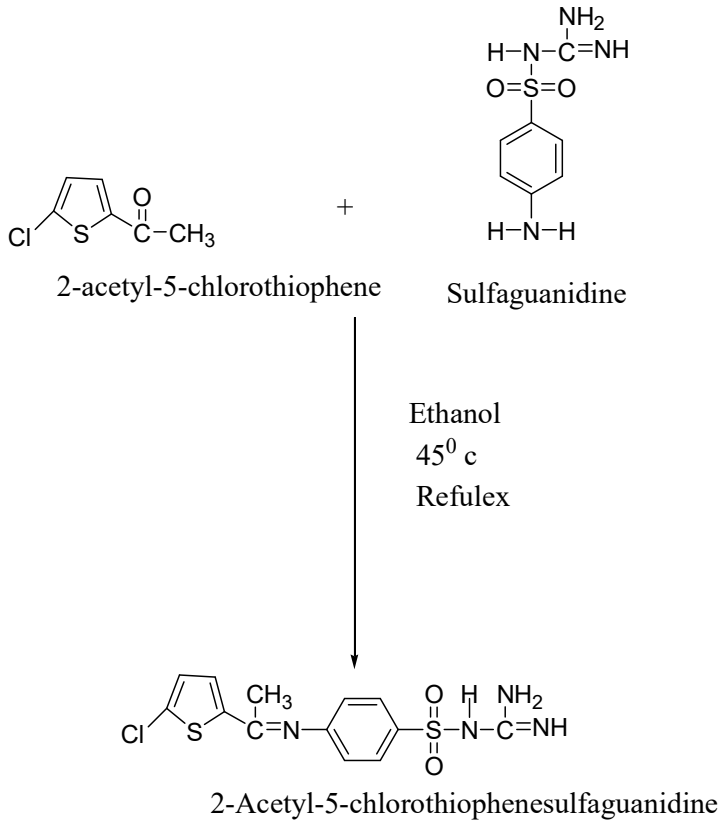


Fig.1. Scheme of 2-Acetyl-5-chlorothiophene sulfaguanidine (2-Ac-5-ClThSG)

Formation of complex: The ethanolic solution of 2-Ac-5-ClThSG was mixed with an ethanolic solution of $CuCl_2.2H_2O$ in a vigorous manner to create the copper (II) complex, which was prepared at a 1:2 ratio. The resulting mixture was heated to sixty degrees celsius under reflux while being stirred for four hours. After that, it was allowed to cool and evaporate into its third volume. After isolating the resulting deep green complex, vacuum-dry it over anhydrous calcium chloride and clean it with ethanol.

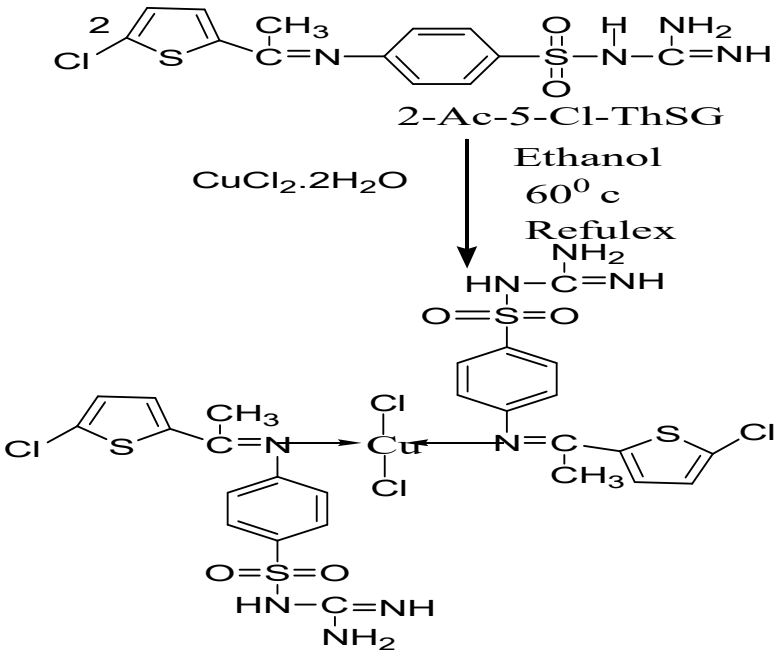


Fig.2.- Copper (II) complex of 2-Ac-5-ClThSG ligand

Results and Discussion

The Cu(II) complex's and the ligand's infrared spectra were obtained using the KBr pallet.The absence of ketonic and amino groups in the condensation product of 2-acetyl-5-chlorothiophene and sulfaguanidine and presence υ(C=N) (1625 cm^{-1}) group is indicative of the Schiff base formation as shown in infrared spectral studies. The complex spectra show a ν (C=N) band in the 1614–1620 cm^{-1} region that moves to a lower side number to indicate that the nitrogen atom is the mechanism via which the ligand and metal coordinate. In analyzing the creation of the new peak in the region 510-560 cm-1 assigned to υ $^{Cu\leftarrow N}$, take into account the bonding of the copper ion to N atoms. [26]

Elemental analyses-

On the C, H, N and S elemental analyzers, elemental analysis was performed using a microanalytic approach. Using a melting point instrument, the melting points of the 2-Ac-5-ClThSG and Cu(II) complex were determined to be 175^0C and 214^0 C, respectively.

Table-1: Elemental analyses

Cyclic voltammetric studies of 2-acetyl-5-clorothiophene sulfaguanidine

CV measurements were carried out using a computer-controlled Digital Constant Current Source. The electrode assembly used for these experiments was incorporated with an

S.No.	Ligand/ complex (M.Wt.)	Colour	Yield(%)	Elemental analysis(%): found (cal.) C	H	N	S	Cu
1.	$C_{13}H_{13}ClN_4O_2S_2$ (356.58)	White	72	43.75 (43.70)	3.67 (3.65)	15.70 (15.66)	17.97 (17.92)	
2.	$C_{26}H_{24}Cl_4CuN_8O_4S_4$ (848.15)	Deep green	66	36.82 (36.76)	3.09 (3.06)	13.21 (13.19)	15.12 (15.09)	7.49 (7.46)

electrochemical cell with a three-electrode configuration system comprising of the working electrode (GCE), reference electrode (Ag/AgCl/KCl) and a platinum wire (auxiliary electrode). Electrochemical observations were done in a variety of solvents, such as ethanol, acetone, and DMF, utilizing phosphate and Britton-Robinson (BR) buffers at different pH values. The study aimed to examine how factors such as solvent type, buffer composition, scan rate, and pH influence the redox behavior of the compound. The experimental setup involved 10 ml of a test solution, comprising 1 ml of a 1 $\times 10^{-2}$ M of the 2- Ac-5-ClThSG and 9 ml of appropriate buffer of selected pH. Cyclic voltammetry was conducted at varying scan rates of 50, 100, 150, 200, and 250 mV/s within a potential window ranging from +1000 mV to -1600 mV. The peak potentials (Ep) and peak currents (Ip) for each observed peak, along with the kinetic parameters determined using equations 1-3, are detailed in Tables 2-5.[27]

$$\left|E_p - E_{p/2}\right| = \frac{1.857RT}{\alpha_n F} = \left(\frac{47.7}{\alpha_n}\right) mV \quad (1)$$

$$I_p = 3.01\times10^5 n(\alpha_n)^{1/2} A C D_0^{1/2} v^{1/2} \quad (2)$$

$$E_P = -\frac{RT}{\alpha_n F}\left[0.78 + \ln\left(\frac{D_0^{1/2}}{k^\circ_{f,h}}\right) + \ln\left(\frac{\alpha_n F v}{RT}\right)^{1/2}\right] \quad (3)$$

Table 2. Voltametric parameters of 1mM 2-acetyl-5-chlorothiophenesulfaguanidine in acetone-phosphate buffer.

pH level	Scan rate (mVs^{-1})	Cathodic peak potential	Cathodic Peak current	Half peak	Cathodic peak current	Charge transfer	Diffusion coefficient	Rate constant ($cm.s^{-1}$)

		(mV)	(µA)	potential (mV)	/ Scan rate$^{1/2}$	coefficient	× 10^3(cm^2s^{-1})	
5	50	-872	6.80	-750	0.96	0.39098	9.68108	3.15E-08
	100	-915	12.93	-762	1.29	0.29264	15.04558	9.24E-07
	150	-940	15.8	-770	1.29	0.29264	15.01142	1.03E-06
	200	-960	17.7	-779	1.25	0.26354	15.3466	2.52E-06
	250	-969	19.1	-781	1.20	0.25372	15.57023	3.7E-06
7	50	-925	10.70	-755	1.51	0.318	16.89127	3.07E-07
	100	-931	10.73	-771	1.07	0.29813	12.37012	5.87E-07
	150	-972	18.37	-782	1.49	0.25105	18.84346	3.71E-06
	200	-975	21.03	-842	1.48	0.35865	15.63025	6.93E-08
	250	-980	19.42	-789	1.22	0.24974	15.47078	3.89E-06
8.2	50	-930	11.04	-770	1.56	0.31382	17.59136	3.47E-07
	100	-972	14.0	-775	1.40	0.24213	17.90939	3.96E-06
	150	-976	15.73	-784	1.28	0.24844	16.21995	3.37E-06
	200	-977	18.80	-785	1.32	0.24844	16.78843	3.99E-06
	250	-982	21.05	-795	1.33	0.25508	16.59285	5.05E-06

Table 3. Voltammetric parameters of 1mM 2-acetyl-5-chlorothiophenesulfaguanidine in DMF-phosphate buffer.

pH level	Scan rate (mVs^{-1})	Cathodic peak potential (mV)	Cathodic peak current (µA)	Half peak potential (mV)	Cathodic peak current/ Scan rate$^{1/2}$	Charge transfer coefficient	Diffusion coefficient×10^3 (cm^2s^{-1})	Rate constant ($cm.s^{-1}$)
5	50	-924	19.20	-808	2.71	0.41121	26.65395	1.95E-08
	100	-936	25.10	-815	2.51	0.39421	25.16443	3.9E-08
	150	-946	30.4	-823	2.48	0.3878	25.09003	5.13E08
	200	-953	34.2	-825	2.41	0.37266	24.93629	9.11E08
	250	-954	38.4	-832	2.42	0.39098	24.4495	5.1E-08
7	50	-949	21.7	-852	3.60	0.49175	27.54734	7.5E-10
	100	-988	28.3	-862	2.83	0.37857	28.9528	3.61E-08
	150	-990	32.8	-872	2.67	0.40424	26.51464	1.51E-08

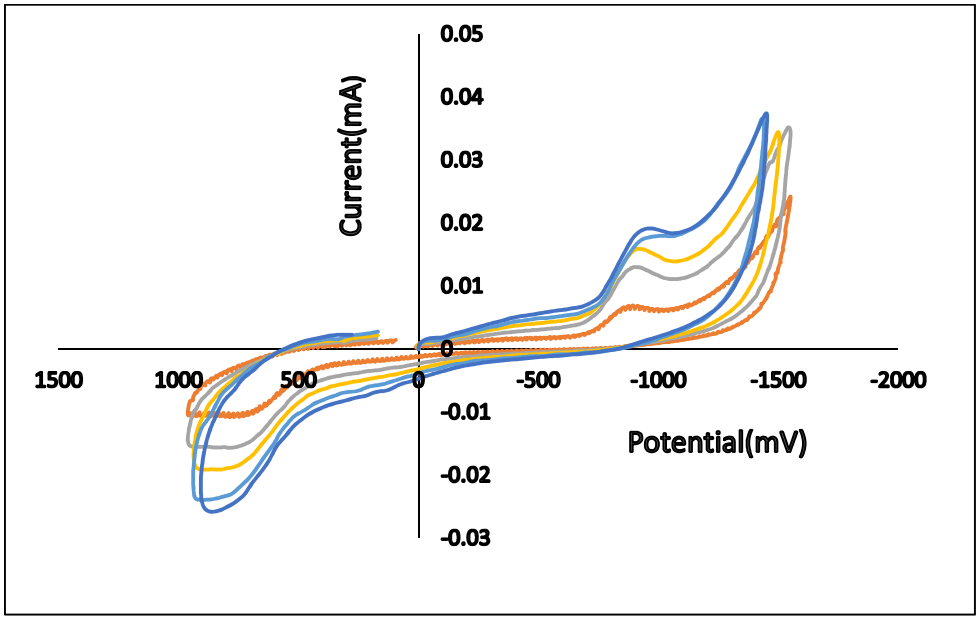
	200	-1000	38.1	-875	2.69	0.3816	27.45257	3.62E-08
	250	-1026	39.7	-880	2.51	0.32671	27.65136	2.3E-07
8.2	50	-1042	22.2	-936	3.13	0.45	29.46042	7.04E-10
	100	-1114	25.0	-955	2.5	0.30084	28.69124	1.45E-07
	150	-1120	31.5	-956	2.57	0.29085	30.01978	2.55E-06
	200	-1177	40.6	-962	2.87	0.22186	38.36619	4.21E-06
	250	-1178	45.4	-975	2.87	0.23498	37.28615	2.56E-06

Table 4. Voltammetric parameters of 1mM 2-acetyl-5-chlorothiophenesulfaguanidine in acetone BR buffer.

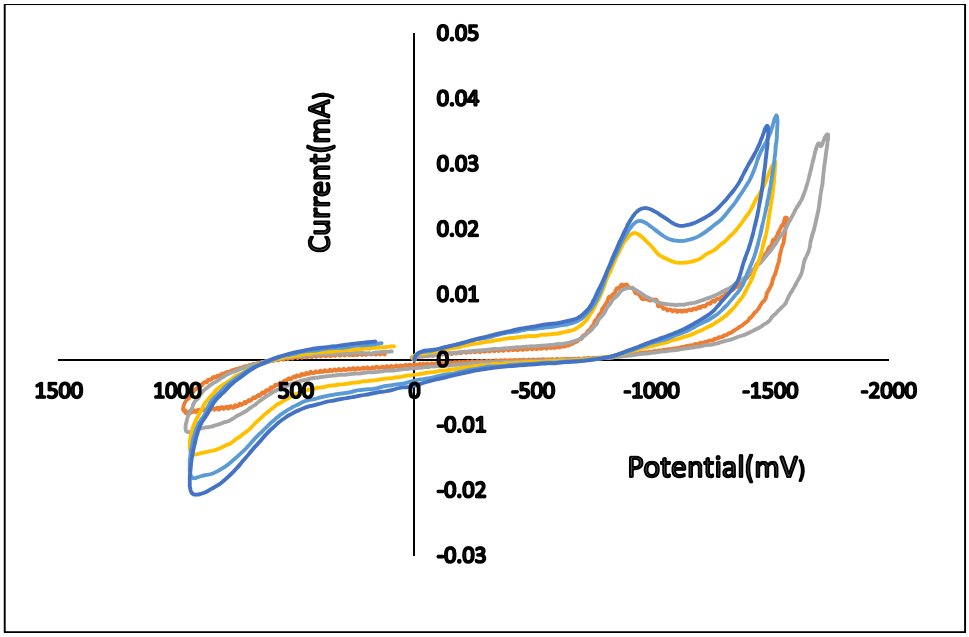
pH level	**Scan rate (mVs^{-1})**	**Cathodic peak potential (mV)**	**Cathodic peak current (µA)**	**Half peak potential (mV)**	**Cathodic peak current / Scan rate$^{1/2}$**	**Charge transfer coefficient**	**Diffusion coefficient$\times10^3$ (cm^2s^{-1})**	**Rate constant ($cm.s^{-1}$)**
5	50	-900	24.0	-803	3.3941	0.44579	31.99914	8.93E-09
	100	-935	32.2	-807	3.22	0.3816	32.81171	8.41E-08
	150	-957	35.6	-814	2.90	0.3417	31.30106	2.99E-07
	200	-970	36.1	-815	2.5526	0.30774	28.96526	8.73E-07
	250	-993	39.3	-819	2.4855	0.27414	29.88266	2.65E-06
7	50	-930	18.1	-810	2.5597	0.3975	25.55655	2.75E-08
	100	-960	25.6	-815	2.56	0.32897	28.09564	3.15E-07
	150	-965	26.5	-820	2.16	0.32897	23.74648	3.06E-07
	200	-970	28.1	-824	1.98	0.31671	21.88201	3.32E-07
	250	-992	30.1	-840	1.90	0.31382	21.39111	3.42E-07
8.2	50	-935	16.6	-812	2.34	0.3878	23.72992	3.31E-08
	100	-975	28.0	-840	2.8	0.35333	29.65138	1.13E-07
	150	-980	31.0	-850	2.53	0.36692	26.30314	6.95E-08
	200	-987	32.0	-886	2.26	0.47228	20.72585	1.43E-09
	250	-996	33.0	-890	2.08	0.45	19.58461	2.34E-09

Table 5. Cyclic voltammetric data for 2-Ac-5-ClThSG in acetone, ethanol and DMF.

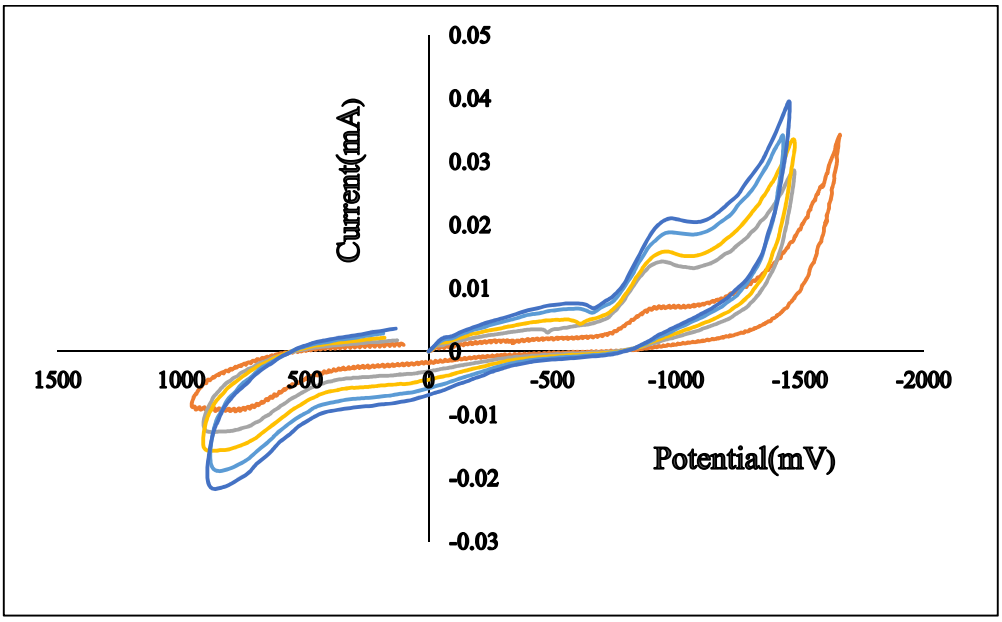
pH level	Scan rate (mVs^{-1})	Cathodic peak potential (mV)	Cathodic peak current (µA)	Half peak potential (mV)	Cathodic peak current / Scan rate$^{1/2}$	Charge transfer coefficient	Diffusion coefficient $\times 10^3$ (cm^2s^{-1})	Rate constant ($cm.s^{-1}$)
Acetone	50	-930	11.07	-770	1.56	0.31382	17.59136	3.47E-07
	100	-972	14.0	-775	1.40	0.24213	17.90939	3.96E-06
	150	-976	15.73	-784	1.28	0.24844	16.21995	3.37E-06
	200	-977	18.80	-785	1.32	0.24844	16.7884	3.93E-06
	250	-982	21.05	-795	1.33	0.25508	16.59285	5.05E-06
Ethanol	50	-993	17.7	-830	2.51	0.29264	29.24238	5.85E-07
	100	-1025	27.40	-859	2.74	0.28735	32.17526	5.47E-07
	150	-1034	28.45	-861	2.32	0.27572	27.8455	1.16E-06
	200	-1068	33.38	-878	2.36	0.25105	29.6529	2.64E-06
	250	-1085	34.30	-885	2.16	0.2385	27.961	3.9E-06
DMF	50	-1042	22.2	-936	3.13	0.45	29.46042	7.04E-10
	100	-1114	25.0	-955	2.5	0.30084	28.69124	1.45E-07
	150	-1120	31.5	-956	2.57	0.29085	30.01978	2.55E-06
	200	-1177	40.6	-962	2.87	0.22186	38.36619	4.21E-06
	250	-1178	45.4	-975	2.87	0.23498	37.28615	4.56E-06



(I)

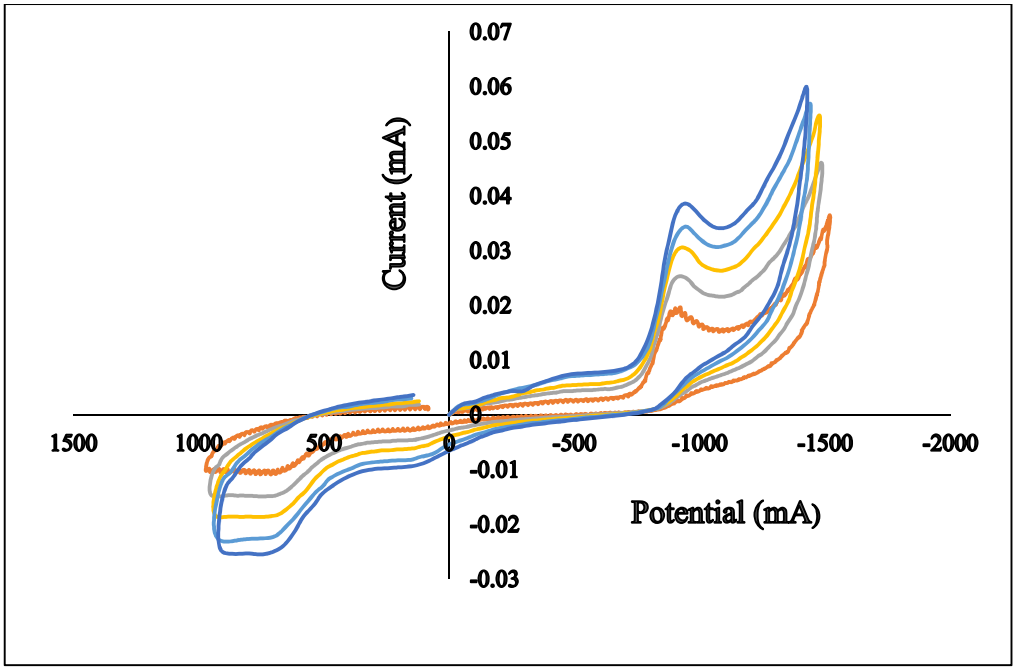


(II)

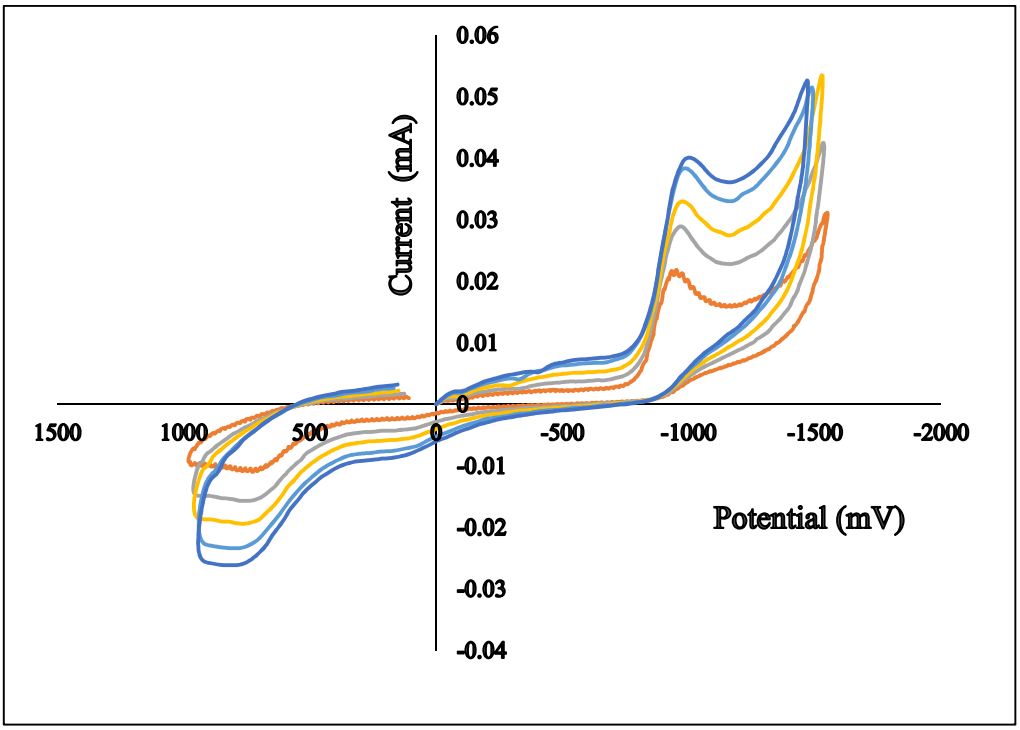


(III)

Fig. 3 Voltammetric curves of 1mM 2-Ac-5-ClThSG in acetone-phosphate buffer at (I) pH 5 (II) pH 7 (III) pH 8.2


Current (mA)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
-0.03
1500
1000
500
0
-500
-1000
-1500
-2000
Potential (mA)

(I)


Current (mA)
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
-0.03
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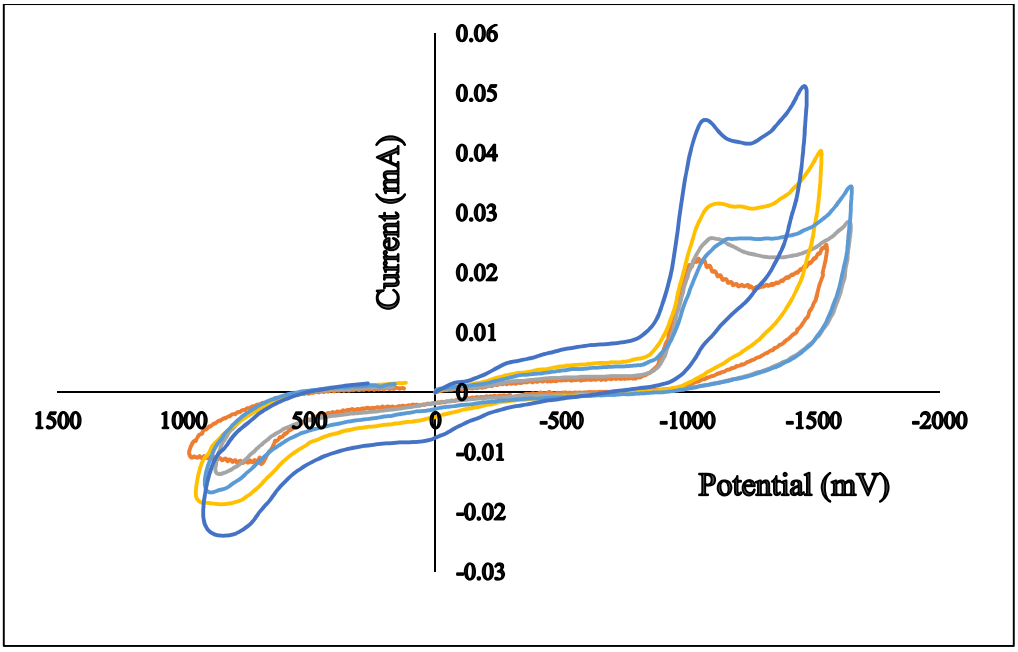
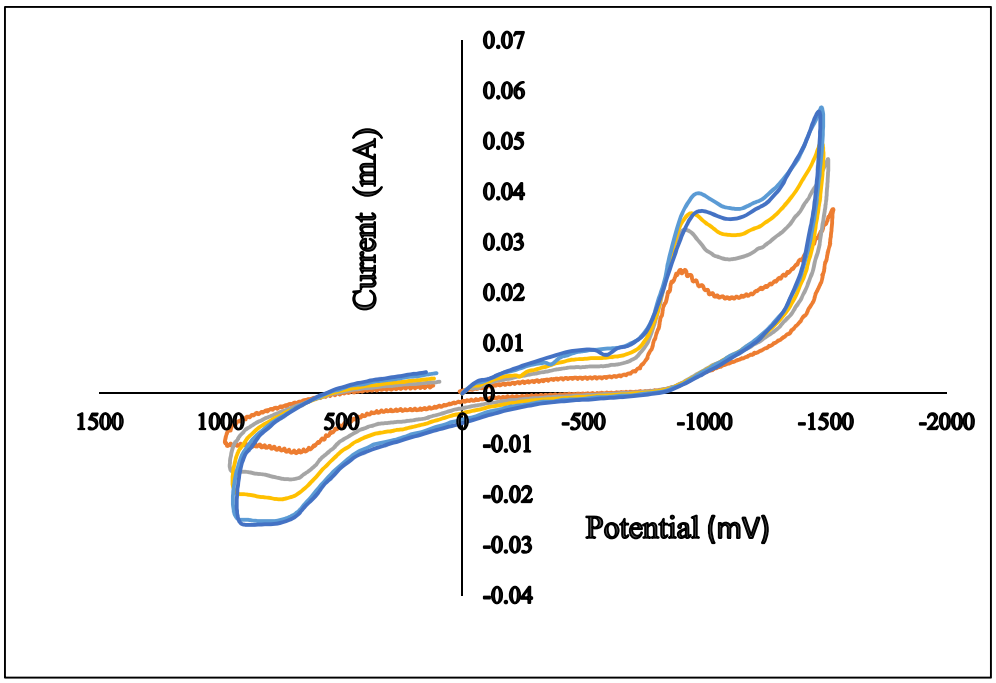
1500
1000
500
0
-500
-1000
-1500
-2000
Potential (mV)

(II)

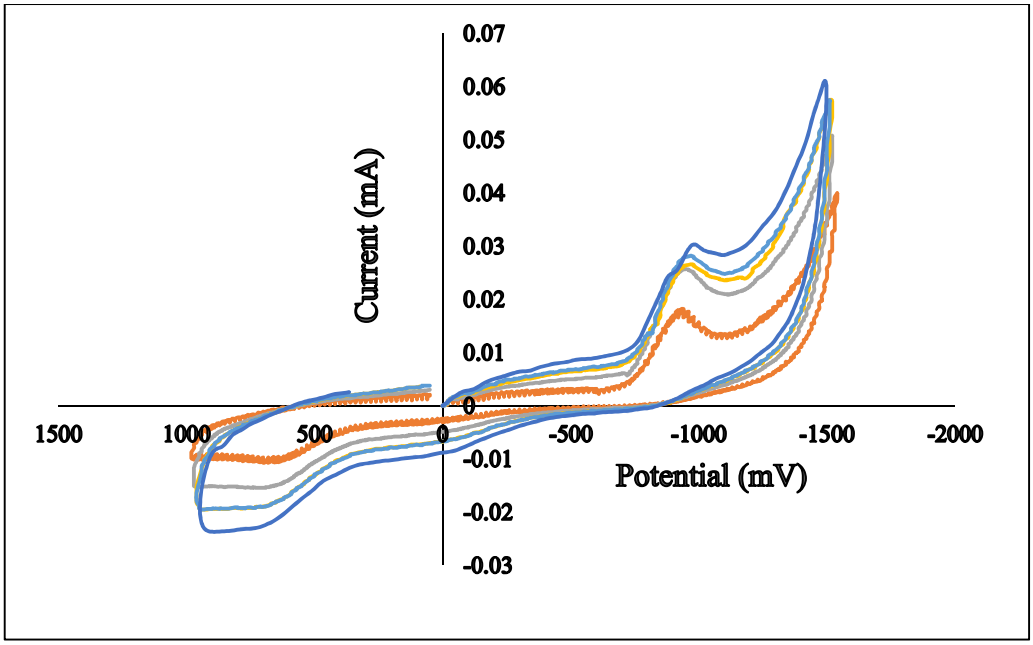


(III)

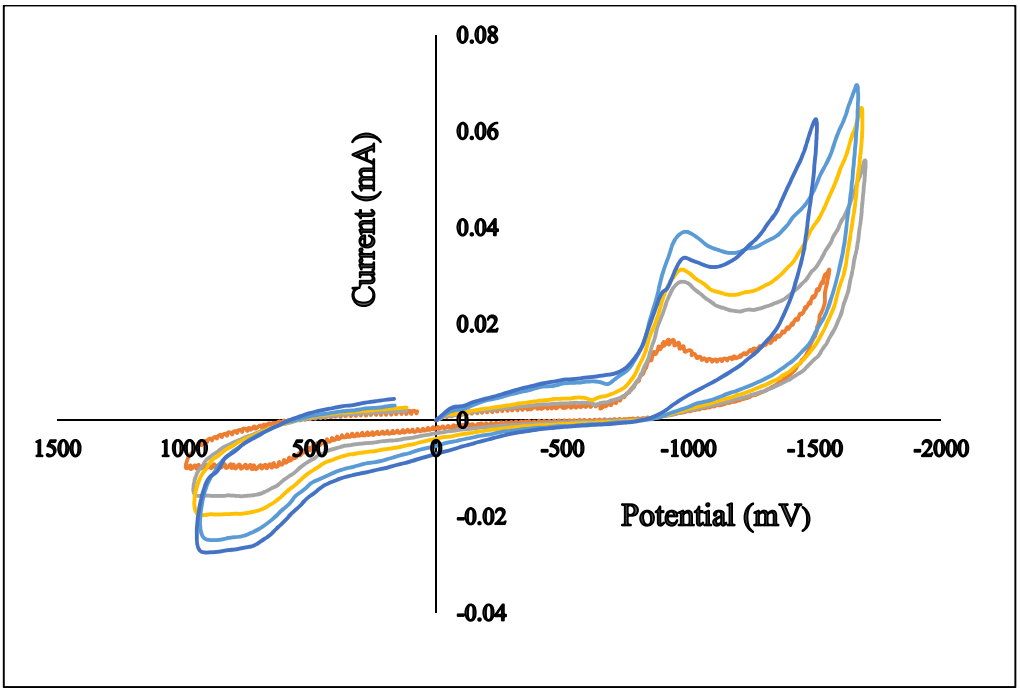
Fig. 4 Voltammetric curves of 1mM 2-Ac-5-ClThSG in DMF phosphate-buffer at (I) pH5 (II) pH 7 (III) pH 8.2



(I)



(II)



(III)

Fig. 5 Voltammetric curves of 1mM 2-Ac-5-ClThSG in acetone-BR buffer at (I) pH 5 (II) pH 7 (III) pH 8.2

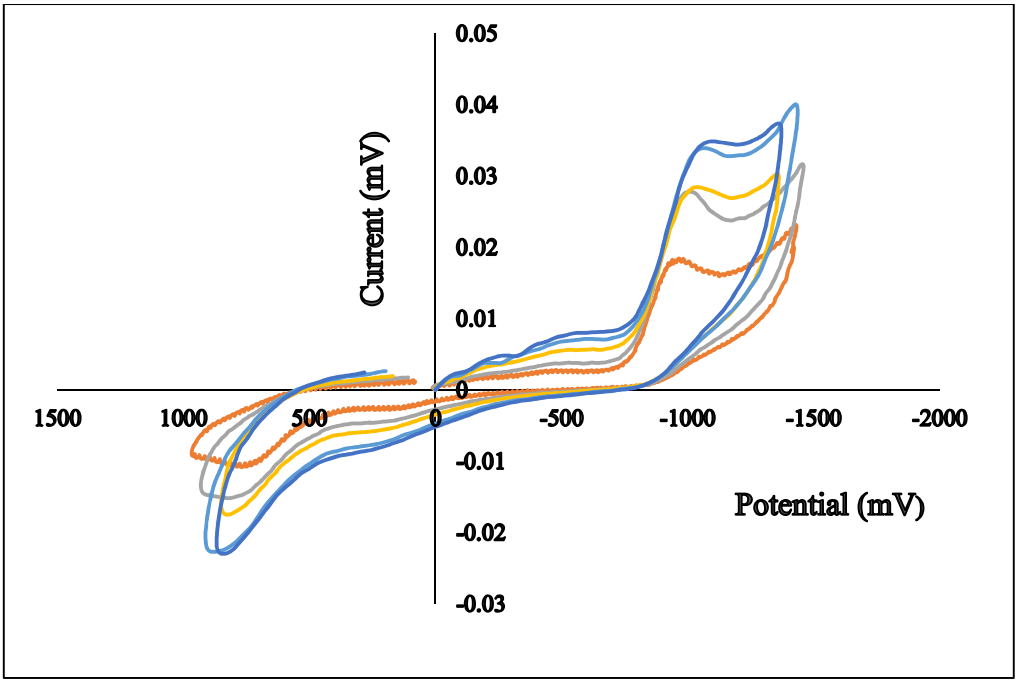


Fig. 6 Voltammetric curves of 1mM 2-Ac-5-ClThSG ethanol-phosphate buffer at pH 8.2

Effect of scan rate on electrochemical characteristic of 2-Ac-5-ClThSG

The scan rate was altered across all cyclic voltammograms, ranging from 0.050 V/s to 0.250 V/s. As the scan rate increased, the cathodic reduction potential shifted towards more negative side, indicating the irreversibility of the electrochemical process. Variation of the reduction potential (Epc) linearly with respect to the natural logarithm of the scan rate (lnv) further supports the irreversible nature of the reduction process. At higher scan rates, a larger shift in peak potential was observed. The data presented in Tables 2 through 4 suggest that these electrochemical processes are controlled by diffusion under the given conditions[28-29]. Furthermore, the cathodic peak current (Ipc) showed an increase as the scan rate was raised.

Effect of pH of medium

Cyclic voltammetric studies of the effect of pH on the reduction of the 2-Ac-5-ClThSG were carried out in order to relate them to the CV data obtained.The peak potential (Epc) valus of 2-Ac-5-ClThSG have been observed in three distinct pH of the test solution. Peak potential values on 50 mV/s scan rate shifted from -924 mV at pH 5, to -949 mV at pH 7 and further shifted to -1042 mV at pH 8.2. On a 250 mV/s scan rate, Epc values shifted from -954 mV at pH 5 to -

1026 mV at pH 7, and further shifted to -1178 mV at pH 8.2 (table-3). Same results are also observed in tables 2 and 4. It is deduced from this behavior that a protonation takes place[30].

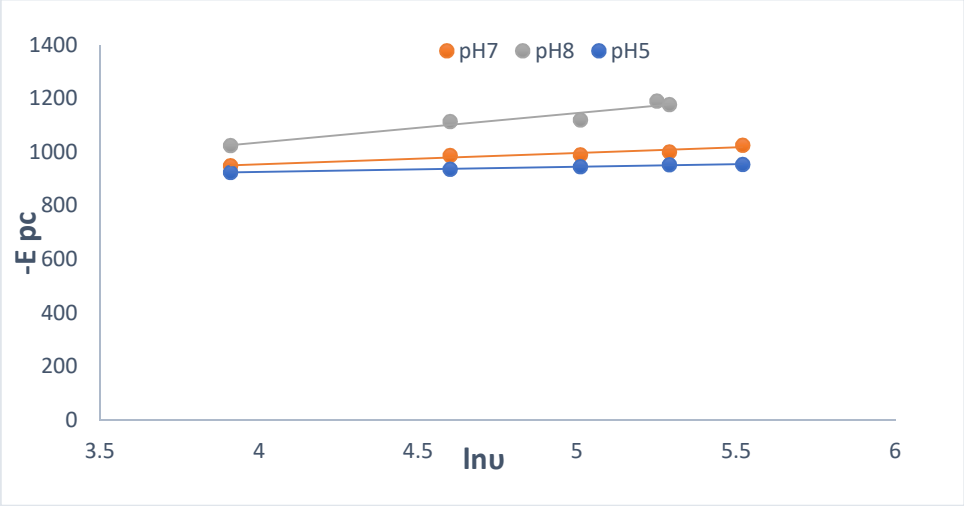


Fig-7. Graph of peak potential against natural logarithm of scan rates: pH 5, 7, and 8.2

Effect of solvents and buffers on electrochemical parameters of 2-Ac-5-ClThSG

In the present investigation, it was observed from table 5, the reduction peak potentials are -930 in acetone, -993 in alcohol, -1042 in DMF an applied scan rate 50 mV/sec. The cathodic shift in the reduction potentials on going from acetone to DMF is attributed to the solvent polarity, steric factor, dielectric constant, and viscosity[31-32]. Similar observations are reported on other scan rates (fig. 8).

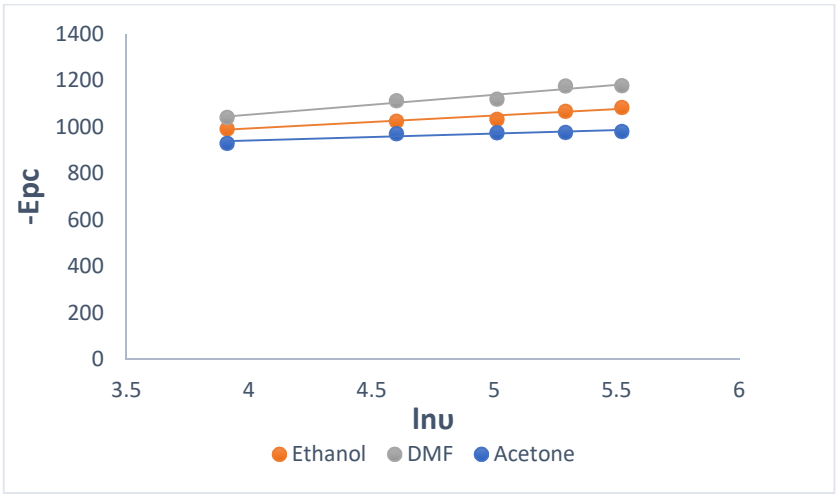


Fig. 8 Peak potential vs natural logarithm for 1mM 2-Ac-5-ClThSG in different solvents with phosphate buffer

The nature of the buffer system used, at a fixed pH has impacts on the electrochemical reduction of 2-Ac-5-ClThSG. The results showed that in the phosphate buffer, the cathodic peak potential

(Epc) values were -925 mV at a scan rate of 50 mV/s and -980 mV at 250 mV/s. In contrast, the Britton-Robinson buffer exhibited Epc values of -930 mV at 50 mV/s and -992 mV at 250 mV/s at pH 7. These findings indicate that the Britton-Robinson buffer has more negative cathodic peak potentials compared to the phosphate buffer at the same pH levels and scan rates. This suggests that the polarity of the buffer solutions has a significant effect on the electrochemical reduction process[33-34], as highlighted in Tables 2 and 4.

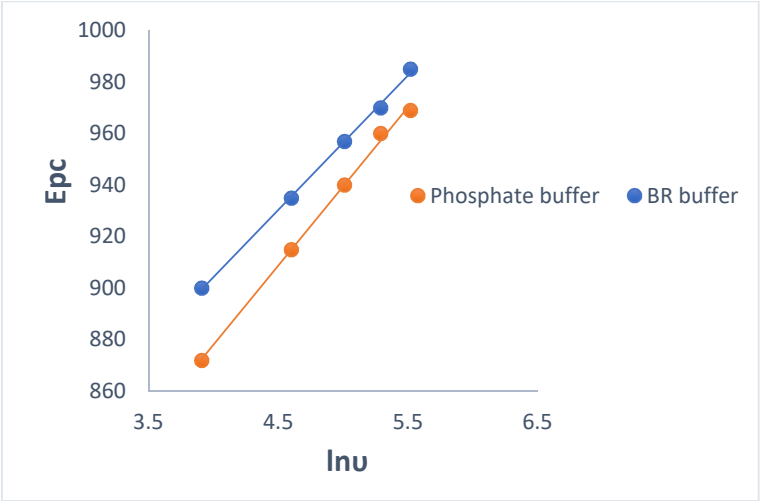


Fig-9. Peak potential vs natural logarithm for 1mM 2-AC-5-ClThSG in different two types of buffers

CV studies of coordination compound of Cu(II) with 2-Ac-5-ClThSG

The cyclic voltammogram of 2-Ac-5-ClThSG copper (II) in DMF using $NaClO_4$ as supporting electrolyte (fig. 10). The cyclic voltammograms indicated negative potential values for the complex, ranging between -0.47 and -0.58 volts. A corresponding anodic wave appeared during the reverse scan, occurring between -0.01 and 0.073 volts, with peak separation (ΔEp) varying from 0.460 to 0.512 volts (table 6). The redox reaction is attributed solely to the copper ion, as no anodic or cathodic peak was shown for the ligand in the potential window chosen for the copper complex. Additionally, a quasi-reversible peak in the cyclic voltammogram corresponds to the conversion between Cu(II) and Cu(I) at a specific potential. The mechanism is characterized by a one-electron transfer, as indicated by the ratio of anodic to cathodic peak currents (Ipa/Ipc)[35-37] being less than one. Furthermore, a linear relationship between the square of the scan rates ($v^{1/2}$) and the cathodic peak current (Ipc) was observed (Fig. 11), supporting the idea that diffusion control predominantly governs these electrochemical processes.

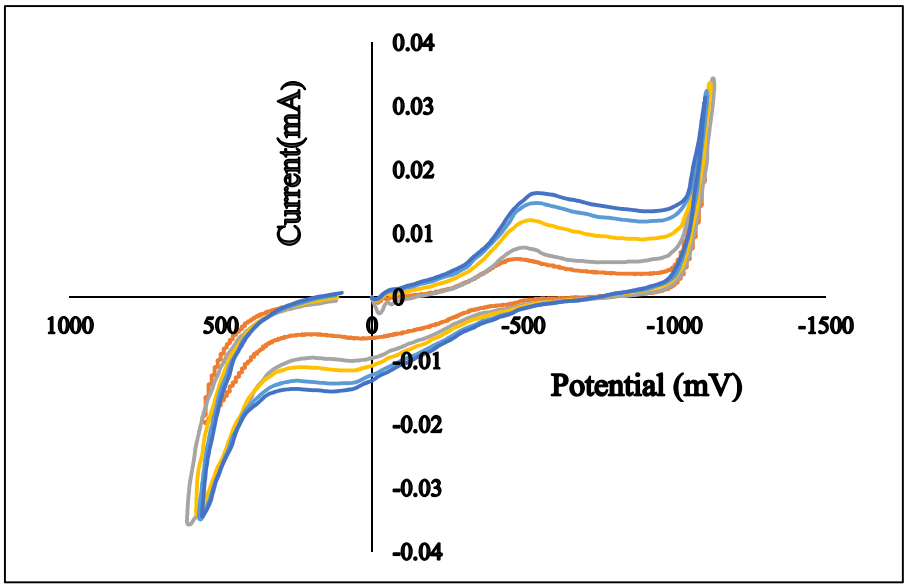


Fig. 10 Voltammetric curves of 1 mM Cu complex of 2-Ac-5-ClThSG

Table 6. Voltametric characteristic of 1mM Cu (II) complex.

Scan rate (mVs^{-1})	**Cathodic peak potential (mV)**	**Anodic peak potential (mV)**	**Peak separation (mV)**	**Half peak potential (mV)**	**Cathodic Peak current (µA)**	**Anodic Peak current (µA)**	**Anodic Peak current/ Cathodic Peak current**	**Cathodic Peak current /Scan rate$^{1/2}$**
50	-470	-10	460	-340	6.0	5.8	0.96	0.8485
100	-521	31	490	-371	8.63	8.5	0.98	0.76
150	-537	39	498	-375	12.0	11.2	0.94	0.9797
200	-560	58	502	-378	14.7	13.4	0.95	1.039
250	-585	73	512	-390	16.9	14.5	0.90	1.02

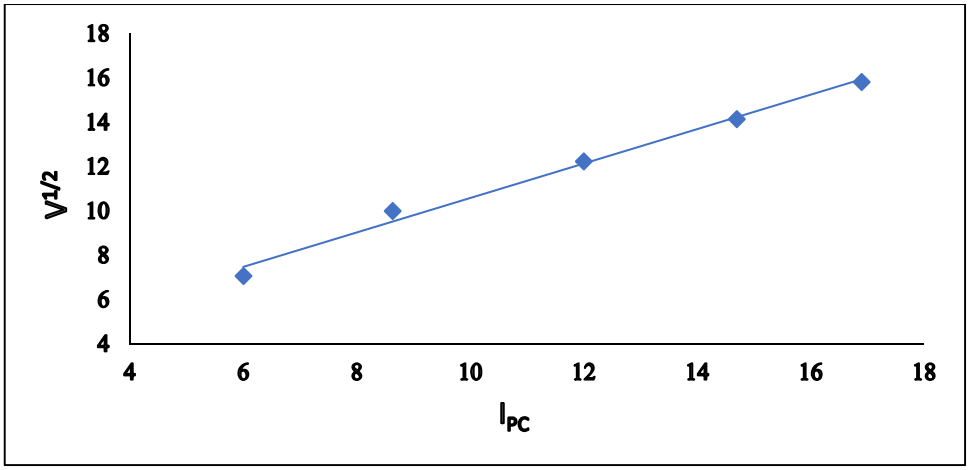


Fig. 11 $\upsilon^{1/2}$ vs Ipc for 1mM Cu(II) complex of 2-Ac-5-ClThSG

Conclusion

Cyclic voltammetric studies demonstrated that the electrochemical behavior of the 2-Ac-5-ClThSG ligand is irreversible and regulated by diffusion, occurring across various pH levels and scan rates ranging from 0.050 V/s to 0.250 V/s. The reduction potential was observed to be influenced by the pH of the experimental solution, the scan rate, and the type of buffers used. As the pH and scan rate increased, both the cathodic peak potential (Epc) and half-wave potential (Ep1/2) shifted towards more negative values. Furthermore, the cyclic voltammograms of the Cu(II) complex indicated a quasi-reversible redox mechanism characterized by one-electron transfer.

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